

LIQUEFACTION PATHWAYS OF BITUMINOUS AND SUBBITUMINOUS COALS AND THEIR INTERMEDIATES

Robert A. Keogh, Liguang Xu, Scott Lambert,
and Burtron H. Davis

Center for Applied Energy Research
University of Kentucky
3572 Iron Works Pike
Lexington, KY 40511

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ABSTRACT

Thermal liquefaction studies of a number of high volatile bituminous coals suggest that these coals have a common liquefaction pathway. Verification of this pathway was confirmed using a single coal and a number of reaction conditions. The addition of a catalyst did not alter the observed thermal pathway. The thermal and catalytic liquefaction pathway obtained for a subbituminous coal was significantly different from the one obtained for the bituminous coals. To investigate ways to alter the bituminous coal liquefaction pathway, the intermediates, asphaltenes and preasphaltenes, were prepared, isolated and liquefied in batch reactors to determine their conversion pathway.

INTRODUCTION

Historically, lumped parameter kinetic models have been used successfully to describe industrially significant processes such as catalytic cracking (1), catalytic reforming (1), and condensation polymerization (2). The same approach has been used in the description of the various liquefaction processes (3,4). A physically realistic and technically viable lumped parameter kinetic model for liquefaction would be of considerable value in the development of pathways, mechanism, and the scale-up of the liquefaction processes.

In the work presented here, the solubility classes obtained from the liquefaction products of the coals were lumped into the following parameters: (a) oils plus gases (O+G), (b) asphaltenes plus preasphaltenes (A+P) and (c) insoluble organic matter (IOM). The lumped parameters used for the liquefaction products obtained from the intermediates asphaltenes and preasphaltenes were: (a) O+G, (b) asphaltenes, and (c) preasphaltenes plus IOM. The lumped parameters were plotted on a triangular diagram for interpretation.

EXPERIMENTAL

The description of the coals used in these study has been given in detail elsewhere (5). All of the liquefaction experiments using the coals were performed in 50 mL batch autoclaves using a hydrogen atmosphere and tetralin as the solvent. Details of the liquefaction runs and the analytical methods used have been described elsewhere (5).

The liquefaction of the intermediates were performed in 25 mL batch autoclaves using the same procedures as those used for the coals.

The intermediates, asphaltenes and preasphaltenes, were obtained from the liquefaction of a Western Kentucky #9 coal and a heavy petroleum resid which contained no asphaltenes. The coal/resid slurry was run in the CAER 1/8 tpd pilot plant using a 1 ℓ CSTR, a reaction temperature of 385°C, a 40 minute residence time and a hydrogen pressure of 2000 psig. The products used for the separation of the asphaltenes and preasphaltenes were obtained from the hot, low pressure separator upon reaching steady state conditions. The intermediates were separated into the solubility classes using the same method as was used in the batch microautoclave experiments. The coal conversion obtained during the steady state operation was 76 wt.% (daf).

RESULTS AND DISCUSSION

The solubility class distributions obtained from the thermal liquefaction of 69 bituminous coals using a single residence time (15 min.) and three reaction temperatures (385°C, 427°C, 445°C) are plotted on a triangle plot in Figure 1. The data suggested a common liquefaction pathway for these coals. The pathway was verified by using a set of reaction temperatures and residence times such that the entire range of conversions were obtained for a single coal (Western Kentucky #6). The data obtained from these experiments are shown in Figure 2. The data in Figure 2 confirmed the thermal pathway suggested from the single residence time data.

The pathway shown in Figure 2 indicates two distinct stages. In the initial coal dissolution stage, the intermediates (asphaltenes plus preasphaltenes) increase with increasing coal conversion. During this stage of coal dissolution, the oil plus gas yields remain fairly constant. It should be noted that the gas produced during this stage of coal dissolution contributes only a small amount to the lumped parameter (O+G). The second stage of the pathway begins after the coal has reached a maximum in conversion (and A+P yield). In this stage the coal conversion remains fairly constant and the major reactions are the conversion of A+P to O+G.

The data obtained from these coals suggest that if a set of conditions could be found which would change the initial stage of the thermal pathway, the process would produce more of the desirable products (oils). One possible method would be to use a catalyst to change the selectivity. A number of catalysts were studied using the Western Kentucky #6 coal. The data obtained from some of these experiments are shown in Figure 3. As can be seen in this figure, the catalytic pathway is similar to the thermal pathway shown in Figure 2. The addition of the catalysts did not change the pathway; however, the catalysts did increase the rate of the production of the intermediates.

Thermal and catalytic data were obtained for a subbituminous Wyodak coal to investigate the effect of rank on the observed pathway. These data are shown in Figure 4. As can be seen in this figure, the pathway obtained is significantly different from the one obtained for the bituminous coals. In the initial and dissolution stage of the pathway, both the A+P and O+G yields increase with coal conversion. In the second stage of the pathway, similar to the pathway of the bituminous coals, the major reaction appears to be

the conversion of A+P and O+G with a small concurrent increase in coal conversion. Also similar to the bituminous coal data, the thermal and catalytic pathway of the Wyodak coal are similar.

The intermediates (asphaltenes and preasphaltenes) were produced, separated and checked for purity to further investigate the pathway of the bituminous coals. The intermediates, both separately and a 50/50 wt.% mixture, were reacted using similar conditions to those used for the coals. The thermal pathway of these samples are shown in Figure 5. The thermal pathway of the coal-derived asphaltenes, as expected, indicates the primary reaction is the conversion of the asphaltenes to oils plus gases. Again, the contribution of the gases to the lumped parameter is small. It appears from these data that the conversion of the asphaltenes follows a similar path both during coal conversion and during the conversion of the isolated intermediate solubility fraction.

The thermal conversion pathway of the preasphaltene intermediate, also shown in Figure 5, was somewhat unexpected. The pathway indicates that the oils are formed slightly faster from the preasphaltenes, presumably through the asphaltene intermediate, than the asphaltenes are formed from the preasphaltenes. However, if the unconverted coal (IOM) is subtracted from the coal conversion products, the points for the conversion of coal and preasphaltenes are similar. Thus, it appears that the conversion of the preasphaltenes follow a similar path during coal conversion and the conversion of the isolated solubility fraction.

The thermal pathway observed for the mixture (50/50 wt.%) of asphaltenes and preasphaltenes is also shown in Figure 5. The pathway defined for the mixture indicates that the two reactants are converted independently. The experimental data and the calculated data based on the conversions of the individual asphaltenes and preasphaltenes runs are similar within experimental error.

SUMMARY

It has been shown that high volatile bituminous coals have a similar reaction pathway and that the addition of a catalyst does not significantly change the observed thermal pathway. The pathway for the bituminous coals indicate that to obtain a significant oil yield, a maximum in the intermediate (A+P) yield (and coal conversion) must be obtained. The thermal and catalytic pathway obtained for a Wyodak coal is significantly different. For this coal, an increase in the asphaltene plus preasphaltene and oils plus gases yield parallel the increase in coal conversion in the initial stage. The thermal conversion pathways of the isolated intermediate solubility fractions were similar to those obtained during coal conversion.

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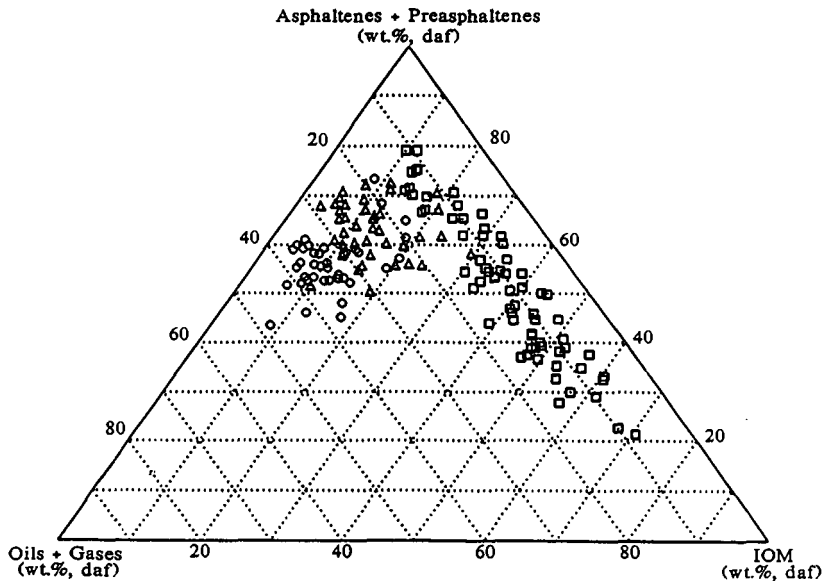


Figure 1. Solubility class distribution of 69 bituminous coals using a 15 minute residence time and three temperatures (\square , 385°C; \triangle , 427°C; \circ , 445°C).

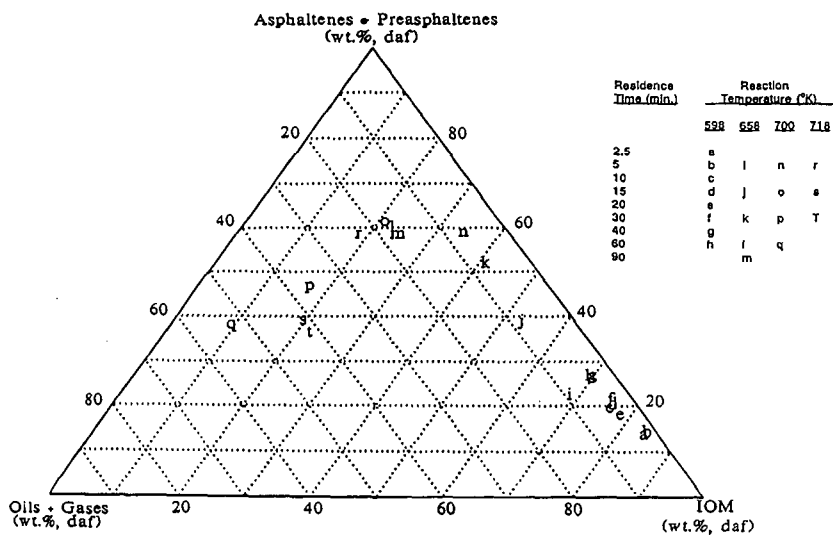


Figure 2. Thermal liquefaction pathway of a Western Kentucky #6 coal.

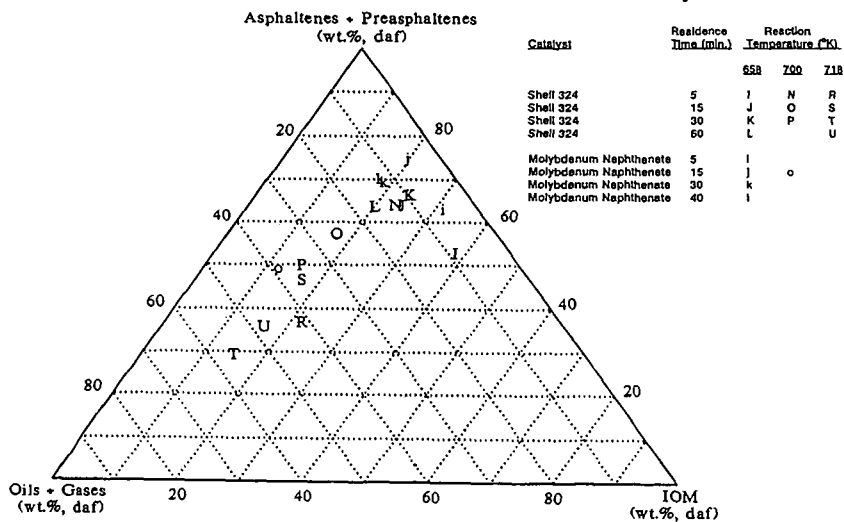


Figure 3. Catalytic liquefaction pathway of a Western Kentucky #6 coal.

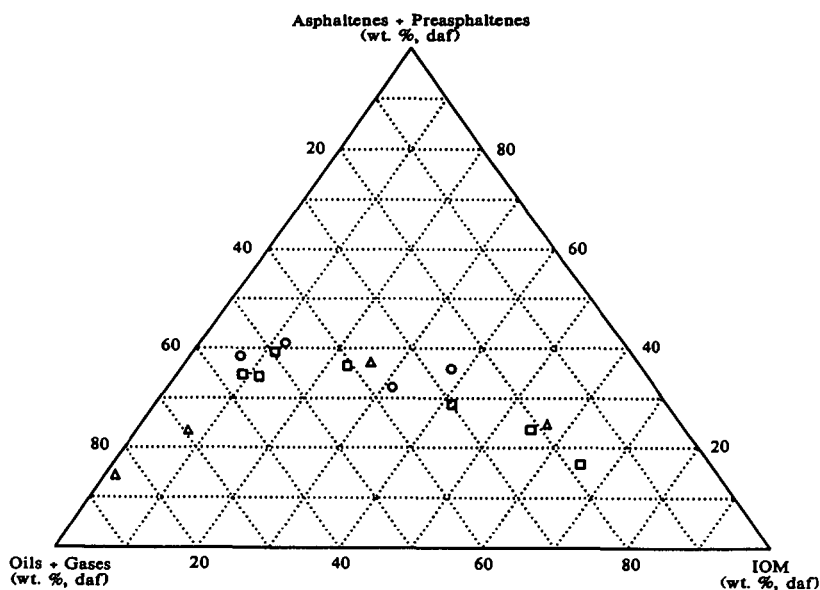


Figure 4. Thermal and catalytic pathway of a Wyodak coal (\square , thermal; \circ , Fe_2O_3 ; \triangle , molybdenum naphthenate).

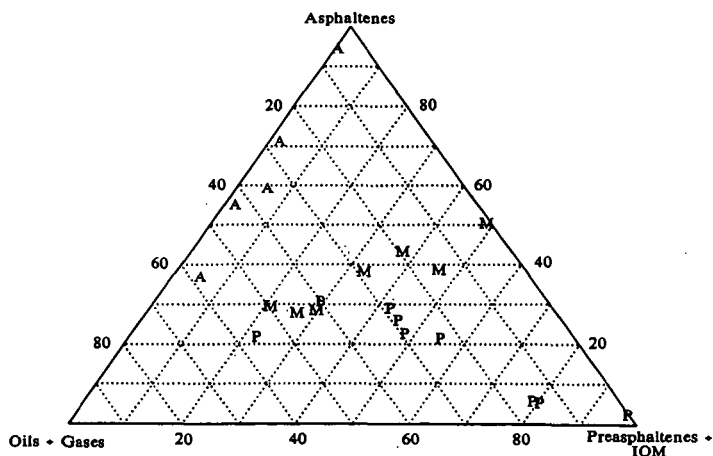


Figure 5. Thermal pathway of bituminous coal-derived asphaltenes (A), preasphaltenes (P) and a 50/50 wt.% mixture of asphaltenes and preasphaltenes (M).